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BOOK NUMBER

A57.23 R31 THE ENIGMA OF SOIL NITROGEN BALANCE SHEETS

By

( surf.) I 2/ F. E. Allison

During the past 50 or more years, many attempts have been made to draw up nitrogen balance sheets for both cropped and uncropped soils. In general, these attempts have met with only mediocre success primarily because cuantitative data are usually not available for some of the items that enter into the calculations.

On the side of income, accurate values for additions in the forms of rainfall, irrigation water, seeds, fertilizers, and manures are usually available. However, if legumes are grown, then there are difficulties. The quantity of nitrogen supplied from the air by rhizobia is not likely to be known very accurately under field conditions but can, of course, be determined under special controlled conditions. Or the experimenter may avoid the problem by growing only non-legumes. With regard to nonsymbiotic fixation, we know very little about the quantities supplied under field conditions because they are commonly too small to be measured. Furthermore, any gains may be more than offset by losses.

On the expenditure side of the balance sheet, we have no difficulty in obtaining accurate values for the nitrogen removed in harvested crops and in animals. As for wind and water erosion, these are usually of only minor importance in carefully planned field studies. Leaching, however, presents a major problem. Seldom do we know what values to assign to this source of loss, and there seems to be a wide divergence of opinion among agronomists as to whether such losses are likely to be large or small.

Ifter the balance sheet has been drawn up, we commonly find that income and outgo do not balance even though account has been made of all known soil nitrogen gains and losses. Usually all of the nitrogen that went into the system has not been recovered. It is assumed that some of it has volatilized. Is this true, and, if so, how is it lost and in what quantity? Only on rare occasions does income exceed outgo, if all of the nitrogen added by legumes is considered. This failure of nitrogen balance sheets to balance constitutes the enigma of this discussion. In a broad sense, we are

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Prepared for delivery at the Soil Microbiology Conference,
Purdue Memorial Union, Lafayette, Indiana, June 21-24, 1954

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concerned with all items that enter into the nitrogen balance sheet; in other words, there are several enigmas. We shall, however, deal primarily with losses by leaching and volutilization, and in a more limited way, with gains of soil nitrogen from the air through channels other than legumes. Such a discussion of nitrogen balance sheets should give us a better idea of why recoveries of nitrogen in the crop are often only 50% of that added as fertilizer.

## Nitrogen Balance Sheet for the Cropped Soils of the United States

When the subject of nitrogen balance sheets is mentioned, we immediately think of the one published in 1936 at New Jersey by Lipman and Conybeare (29). In this study a major attempt was made to account for the income and outgo of soil nitrogen in the United States. I mass of data was assembled and studied, but Lipman emphasized that in many cases cuantitative information was inadequate for arriving at accurate values for the cuantities of nitrogen gained and lost through the various channels. Lipman's nitrogen balance sheet for our cropped soils is shown on slide 1.

Slide 1. Nitrogen Balance Sheet for Harvested Crop Free of United States - Lipman 1936 (367,554, 185 acres)

	Lbs. N per acre per year
Nitrogen additions:	
Rain and irrigation Seeds Fertilizers Manures Symbiotic N fixation Non-symbiotic N fixation	4.7 1.0 1.7 (7.0 in 1951) 5.2 9.2 6.0
Nitrogen losses:	27.8
Harvested crops Erosion Leaching Volatilization	25.1 24.2 23.0 
Net annual loss	44.5 +

This balance sheet is interesting, but it contributes little to the present discussion; because it is incomplete. We need to know the annual decrease in soil nitrogen. Without this figure, we do not know whether all of the nitrogen can or cannot be accounted for; there may have been large losses of nitrogen as gas that are not

mentioned in Lipman's tables. The data do, however, emphasize the large losses due to leaching and erosion. These values should be borne in mind in connection with the later discussion.

A more accurate idea of what is happening to nitrogen in soils can be obtained by studies of individual experiments where soils have been maintained under near-natural conditions, and nitrogen income and outgo measured over a long period of years. In general, such data can be obtained only from lysimeters. Field plot experiments may furnish supplemental information; but, of course, accurate balance sheets cannot be constructed. In occasional pot experiment may also have been performed in such a manner that it supplies valuable information.

Reference will first be made to several lysimeter experiments reported from state experiment stations. The most suitable experiments for this purpose are those:

- 1. Where nitrogenous fertilizers, or manures, were added in considerable cuantity,
- 2. Where no legumes were grown,
- 3. Where all crops and soils were analyzed, and
- 4. Where the experiment was continued for 5 years or longer, thereby reducing the errors due to soil sampling and analysis. In all such experiments erosion is, of course, eliminated.

Il of the available data that meet the above requirements cannot be discussed in the time available; but representative data from the five experiment stations in this country, where the most work of this type has been done, will be considered.

#### Lysimeter Experiments

Experiments at Cornell Experiment Station.—During the period since 1910 several lysimeter experiments have been conducted at the Cornell Station. Concrete tanks were filled with layers of scil corresponding to the natural soil horizon.

In one experiment, reported by Bizzell (7), a sandy loam soil was cropped for 15 years with two vegetable crops each year, followed by a winter cover crop. Nitrogen was added in the form of ammonia or nitrate to each vegetable crop at the time of planting. Slide 2 shows the nitrogen balance sheet.

Slide 2. Recovery of Nitrogen from Ammonium Sulfate and Sodium Nitrate in a 15-year Lysimeter Experiment at Cornell - Big-ell (Vegetable crops plus rye cover)

Bizzell (Vegetable crops	s plus rye c	over)
	fm. sulfate	Sodium nitrate
		acre per year*
Nitrogen sources:		
Rain Fertilizer Soil loss	6 11/3 31	6 143 47
Nitrogen recovery:	180	196
Crops Leachate	94 42	110 46
	136	156
Nitrogen not accounted for	44	40
	% of Avail	lable N
N in crop N in leachate N not accounted for	52 23 24	56 23 20

<sup>\*</sup> Averages of 3 replications

It will be observed that there was a marked decrease in soil nitrogen during the 15-year period even though large quantities were added each year. Furthermore, only a little more than half of the nitrogen added or made available from the soil was recovered in the crop. About half of the remainder was found in the leachate, whereas the other portion was unaccounted for. It is well to bear in mind that the loss occurred in a well aerated sandy loam that was fertilized with excess nitrogen, intensively cultivated, and limed at intervals to keep the pH near 6.0. J. K. Vilson (58) believed that such losses are commonly due to loss of nitrite in the exudate from plants, or as nitrogen gas formed as a result of the reaction of nitrite with amines in plant juices.

Inother interesting Cornell lysimeter experiment using Dunkirk silty clay loam was reported by Bizzell (3). In this experiment timothy was grown for 8 years and sodium nitrate in varying amounts was added in three installments each year. The experimental procedures were

similar to those used in the experiment just discussed. Slide 3 shows the nitrogen balance sheet.

Slide 3. Recovery of Nitrogen in an 8-year Lysimeter Experiment at Cornell - Bizzell (Continuous timothy)

		Lbs. N per acre per year					
N. L	Nos:	<u>l</u> ı & 9:	5 & 10:	6 & 11	8 & 12	_	
Nitrogen additions: Rain Sodium nitrate		6 213	6 155	6 124	6 93	_	
		219	161	130	99		
Nitrogen recovery: Crops Leachate Soil gain		15h 3 17	121 2 14	98 1	78 2 15		
Nitrogen not accounted for		174 45	137 24	118	95 4		
		% of available N					
N in crop N in leachate N not accounted for		70 1 21	75 1 15	75 1 9	79 2 4		

Under continuous timothy the soil showed a gain of about 16 pounds of nitrogen annually. The crop recovered 70 to 79% of the available nitrogen (fertiliger plus rain). There was almost no loss of nitrogen in the drainage water even where 213 pounds were added annually. The small loss that did occur was in the first year before the timothy was well established. Regardless of this, there was an unaccounted-for loss of nitrogen that varied from a negligible amount at the lowest rate of nitrate addition to 45 pounds per acre per year at the highest rate. Bizzell considered the losses to result chiefly from volatilization.

Experiments at Geneva, New York. -- In 1933 Collison and co-workers (14) reported the results of a 16-year lysimeter experiment at Geneva, New York. In these experiments, where no fertilizer was applied, a soil of low fertility and one that was more productive were used. I nitrogen balance sheet for the lysimeters that were kept in a 4-year, timothy-grain rotation is shown on Slide 4.

Slide L. Nitrogen Balance Sheet for 16-Year Lysimeter Experiment at Geneva, N. Y. -- Colliscn (Timothy 2 yrs., barley, wheat)

	Low fertility soil	More fertile soil
77	Lbs. N per acr	e per year *
Nitrogen sources:		
Rain	9	9
Seed	2	2
Soil loss	52	118
	63	129
Nitrogen recovery:		
Crops	44	69
Leachate	8	14
	52	83
Nitrogen not accounted for	11	46
	% of avail	able N
N in crop	70	53
N in leachate	13	11
N not accounted for	17	36

<sup>\*/</sup>verages of 2 replications

Both soils lost considerable nitrogen during the 16-year period, and this loss increased as soil fertility increased. It is a little surprising that even though no fertilizer or manure was added, there was a loss of 17 to 36% of the nitrogen available to the crop. This unaccounted-for nitrogen was more than twice the amounts recovered in the drainage waters. The author concludes that the only explanation for the large nitrogen deficits is that nitrogen escapes to the atmosphere.

Experiments at Windsor, Connecticut. -- Rather extensive lysimeter experiments (22, 37, 38, 39), using Merrimac sandy loam, have been reported from the tobacco station at Mindsor, Connecticut. In one experiment, various nitrogen sources were applied to tobacco grown continuously for 10 years. The nitrogen recovery data are shown on Slide 5.

Slide 5. Nitrogen Balance Sheet for 10-Year Lysimeter Experiment at Windsor, Conn. -- Morgan (Continuous tobacco)

Fertilizer Sources								
	Three nitrates:			organis fertilizers	None (1 rep.)			
	•	Ting.	N per acre	per year				
Nitrogen sources Rain Fertilizers Soil loss	14 200 19	200 -	200	4 200 <b>-</b>	4 0 36			
	223	204	204	204	40			
Nitrogen recover Crops Leachate Soil gain	93 123	73 108 6	88 88 <b>1</b> 0	79 82 19	20 31			
N not accounted	216 for 7	187 17	186 18	180 24	51 (ll gain)			
		% of	available	N				
N in crop N in leachate N not accounted	ί <sub>1</sub> 2 55 for 3	36 53 8	43 43 9	39 40 12	50 78			

In this experiment with a very sandy soil that was heavily fertilized with nitrogen, it will be observed that usually more of the added nitrogen was recovered in the drainage water than in the crop. Nearly all of the added nitrate was accounted for but there was an average loss of about 10% of the nitrogen added in other forms.

In a similar experiment, calures was added to cylinders at the rate of 200 pounds of nitrogen per acre per year for 10 years and various cropping systems compared. Slide 6 shows the nitrogen recovery data.

Slide 6. Nitrogen Balance Sheet for 10-Year Lysimeter Experiment at Mindsor, Conn. -- Morgan (Tobacco or grass)

4 4 p = 41 H3		150				
		lized wi			:No nitro	gen
			Tobacco		: :	:
	:		and oat			Grass:
	:Isllow:	Tobacco:	cover	sod	:Tobacco:	sod :
	•	Lbs. N	per ac	re per	year*	
Nitrogen sources						
Rain	L	1	L	4	<u> </u>	1,
Fertilizer	200	200	200	190	Ō	0
Soil loss-	67	28	. 2	-	51	40
	271	232	206	194	55	44
Nitrogen recovery	·					
Crops	0	90	94	77	19	16
Leachate	225	97	1.8	28	29	6
Soil gain				8		
	225	187 -	142	113	48	22
N not accounted for	46	45	6L	81	7	22
			f avail	able N		
				4* - 4		
N in crop	-	39	46	40	34	36
N in leachate	83	L2-	. 23	1 <u>4</u>	53	14
N not accounted for	17	19	31	42	13	50

\* Iverages of two replications

The average percentage of added nitrogen plus that released from the soil that was unaccounted for varied between 17 and 12% for the fertilized lysimeters, and between 13 and 50% for the unfertilized scils. It is especially surprising that the lowest recovery was with grass sod. Most investigators have observed little or no losses with scd crops and some marked gains have been reported. The recoveries of added nitrogen were the same where tobacco was grown as where the soil was kept fallow. In other lysimeters, where mixed sources of nitrogen were used instead of calurea, the % recoveries were similar. Both the winter cover crop and grass markedly reduced the nitrogen in the leachate but did not improve the balance sheet.

Experiments at Knoxville, Tennessee. -- Lysimeter experiments on the recovery of fertilizer nitrogen from soils have been reported from the Tennessee Experiment Station. In the two experiments of most interest in the present discussion, the soils, unfortunately, were not analyzed at the end of the experiments. The recovery of added nitrogen must, therefore, be based on the difference between the nitrogen in the drainage waters from fertilized and unfertilized soils.

In these experiments 989 pounds of nitrogen per acre in the form of nitrate (36), or of ammonium salts (31) were added in a single application to an uncropped clay soil in 6-foot lysimeters. Slide 7 gives the results.

Slide 7. Recovery of Nitrogen from Cumberland Silt Leam at Tennessee - McIntire (Uncropped)

	Nitro	gen in drai	nage water:	5 h n n 4 4 2 2 4 1 1	
		: From-			
	: Lbs.	:Fertilize	r: %	: %	:
•	:per acre	:Lbs.per	recovery	:recovery	:
	:	acre	:	:	:
First expt.*_5 yrs.  No treatment Calcium nitrate Magnesium nitrate Sodium nitrate	68.3 889.8 871.1 987.4	821.5 802.8 919.1	83.1 81.2 93.0	85.8	
Second expt.*-12 yrs. No treatment Ammonium chloride Ammonium phosphate Ammonium sulfate	372.8 1160.1 1111.3 1224.7	787•3 738•5 851•9	79.6 74.7 86.2	80.2	

\*Single additions of 989 lbs. N per acre. 3 replications

The recovery of added nitrate nitrogen averaged 86%, and that of ammonia nitrogen 80%. Loss of a fair percentage of the nitrogen by volatilization is indicated.

All of the experiments discussed previously have dealthwith soils in the humid regions. Similar data from the semi-arid and irrigated regions are sparse. Reference will be made here to only one such experiment, namely, that at Riverside, California.

Experiment at California Station. -- The experiment at California, described by Chapman and co-workers (12), and by Broadbent and Chapman (10), is being conducted in lysimeters that are 10 feet in diameter and 4 feet deep. These were filled with a Sierra loam top soil having a nitrogen content of 0.04%. The data for the six lysimeters that were cropped to Sudan grass for the 15-year period are given on Slide 8.

Slide 8. Nitrogen Balance Sheet for 15-Year Lysimeter Experiment at California -- Chapman and Broadbent (Sudan grass)

		2 =	+ ~	na a			March	tard co	aron .
	•	-	P.5 tons straw: : No cover crop :				turne		
	<u></u>							100:	
	•				200				
:	:	N	_		lbs.	_		Lbs.N:I	DS.N:
			<u> </u>	bs. I	per	а	cre per	year_	
37.4	:		:	:	3	:	:	• 0	:
Nitrogen sources	:	•	:			:	:		
Rain and irrigation •	:	8		8- :			11:	13:	13:
Fertilizer and straw .	:	32		131 :		:	.0:	100:	200:
Soil loss	:_	96	:	96.	71	:	120:	75:	48:
	:		:		3	:	:	:	:
	:	136	:	235 :	316	:	131:	188:	261:
Nitrogen recovery	:		:		:	:	. :	:	:
Crop .	:	84	:	140. :	171	:	87:	139:	192:
Leachate .	:	51	:	73.	,		18:	31:	40:
	-		<u>:</u>	12		<u>:</u>	. :	:	
		135		213 :	284		105:	170:	232:
Nitrogen not accounted	•	エンフ	•	ه ريدے ه	204	:	10).	T10.	<i>L ) L</i> •
for	•	٦	•	20	20	•	26:	18:	20.
101	:		:	22 :				10:	29:
	<u>:</u> _		%	OI 8	evail	ap.			
27. 4	:	10	:	:	1	:	:	1	-1
N in crop	:	62		60 :			66:	74:	74:
N in leachate	:	37	:	31 :	_	:	243.00	16:	15:
N not accounted for	:	1		9:		:	20:	10:	11:
Nitrogen supplied as calcium nitrate; no replication									

In all cases the soil lost much nitrogen and there was failure to account for all of the available nitrogen added or released from the soil. The recovery varied between 80 and 99%. The authors (10) point out that the errors of soil sampling were large. This was due in part to the absence of leaching during the last 5 years of the experiment, which permitted some accumulation and uneven distribution of nitrates. The unaccounted-for nitrogen was presumably volatilized.

In considering lysimeter experiments, it is well to bear in mind that a high degree of accuracy in such experiments is impossible. Chief among the sources of error are the inaccuracies of soil sampling and analysis, and also the errors in the analysis of the leachate. Nevertheless, such experiments do furnish valuable information.

The experiments discussed here bring out the following facts:

1. Crops commonly recovered only 40 to 80% of the nitrogen that was added, or made available, from the soil. Lowrecoveries were usually obtained where large additions of nitrogen were made, where the soils were very sandy, and where the crop was note adequate to keep the nitrogen low.

- 2. The nitrogen content of most soils decreased regardless of how much was added as fertilizer unless the soil was kept in uncultivated crops.
- 3. A large proportion of the nitrogen not recovered in the crop was found in the leachate, but substantial unaccounted-for losses occurred in most lysimeters. Nitrogen gains were few.
- 4. The magnitude of the unaccounted-for nitrogen was largely independent of the form in which the nitrogen was supplied, whether as nitrate, ammonia, or organic nitrogen.
- Unaccounted-for nitrogen was commonly slightly higher in cropped scils than in fallow soils. Fifty-one lysimeters that received nitrogen, and were planted to non-logume crops, showed an average loss of 20% of the total available nitrogen; the corresponding figure for 106 uncropped soils was 12%. The average value is near 15%. A small portion of this loss can be accounted for as due to factors, such as insects and birds, loss of leaves and pollen, leaching of nitrogen from the leaves, and failure to determine total nitrogen rather than only nitrates, in the leachate. On the other hand, any nonsymbiotic nitrogen fixation that may have occurred would increase the 15% loss figure. These data constitute strong evidence that nitrogen losses from normal, well-aerated soils, by volatilization, are not negligible.

The statement is frequently made that lysim ter experiments are too crtificial to show what happens under normal conditions. Drainage losses seem to be much too high, especially if filled lysimeters are used. Although this criticism is doubtless justified in many cases, this fact does not seriously affect the value of the data for use in the present discussion of the nitrogen balance enigma.

Field Experiments at Rothamsted, England. -- In this connection, data from the Broadbalk wheat fields are of interest because rain gauges are located near the plots. Slide 9, taken from Russell's (47) recent book, gives the pertinent information.

Slide 9. Losses of nitrogen from soils at Rothamsted

	Broadbalk wheat plots :Drain:  1865 - 1914 :gauges:  1870-1915,  Plot 3: 7 & 13:Plot 2 B:uncropped:  No :Am.sulfate: Farm: and:  Nitrogen: P and K: manure: untreated
Nitrogen sources	Lbs. N per acre per year
Rain and seed	
	0 : 86 : 201 : 0
Fertilizer or manure	
Soil loss, top 9 in.	: 8 : 3 : - : 26
***	: 15 : 96 : 208 : 31
Nitrogen recovery	
Crop	: 17 : 45 : 50 : -
Leachate	:not deter: not deter: not deter: 27
Soil gain	: : 15 : -
•	: 17 : 45 : 65 : 27
Nitrogen not accounted for	: 2 : 51 : 143 : 4
	: (gain) : :

No replication

On the wheat field, where no nitrogen was added, the nitrogen in the crop accounts for all that was added in the rain plus that released from the soil. There was no appreciable drainage loss under these conditions of low available nitrogen. Where no crop was grown on a similar soil in the drainage gauge, practically all of the released available nitrogen was recovered in the drainage waters. Evidently, under these conditions if a crop was present, it got the nitrogen; otherwise it was lost in the drainage. There is no evidence for gaseous losses of nitrogen at this low nitrogen level, or for nitrogen fixation. One process could, of course, offset the other.

Where nitrogen was added as fertilizer or manure, the curntity not accounted for was large. For ammonium sulfate it was about 50% and for farm manure, at a much higher rate of nitrogen application, it was near 70%. Most of this unrecovered nitrogen was probably lost by leaching just as occurs in lysimeter experiments. In addition, appreciable losses as both ammonia, and as free nitrogen gas, would be expected from the manured plot, and to a lesser extent from those receiving ammonium sulfate.

#### Cylinder Experiment at New Jersey Station

Inother interesting set of experiments that serves as a tie-in between lysimeter and field experiments is the  $\mu$ -year cylinder experiment ( $\mu\mu$ ) conducted at the New Jersey Station. In these experiments there was no provision for catching the drainage waters. The subsoil was merely removed and mixed, the  $\mu$ -foot cylinders put in place, and the subsoil replaced. Fight inches of Penn loam topsoil was then added.

One portion of the cylinders was fertilized regularly with different nitrogen sources, including manure, and cropped to a 5-year rotation of corn, oats, wheat, and timothy. Slide 10 gives the nitrogen recovery data for both the limed and unlimed series.

Slide 10

	not accounted for		Ltrogen recovery: Crop		itrogen sources: Rain Fertilizer or manure 0 .129 Soil loss 62 6				(5-yea:
/	or 52		32	67	5 manure 0 62		Nc : N :Manu	Į.	Since 10. Recovery of Nitrogen from 40-year Cylinder Experiments at New Jersey (5-year rotation: corn, cats, oats, wheat and timothy)
	54		65	140	.129 6		:Sod re:nitr	Limed (PH 5.7-6.7)	very of Nitrogen from 40- Experiments at New Jersey on: corn, cats, cats, whe
67	44	%	61	109	50 54	SqT	:Am.	H 5.7-	trogents,
	47	% of available N	52	98	51 42	Lbs. N per acre per year	n. :I	6.7)	n from New Jej oats,
	45	able	51	92	50 50 37	acre	:Dried::No :blood:: N		40-ye rsey wheat
A	72 61	Z	21 60	74 153	69	per	. No	Unl	ar C and
	19		60		5 5 0 129 69 19	year	: Manu	imed	ylind timo
770	68		36	114	50 59		:Sod ure:nît	Unlimed (PH 4.1-5.2)	er thy)
$\setminus  $	78		26	119	5 5 .51 50 63 66		: Sod :Am. :Dried::No : Sod :Am. :Dried::Manure:nitrate:sulf.:blood:: N :Manure:nitrate:sulf.:bloo	1-5.2)	
	73		32	121	50 66		ried f.:bloo		

In the limed soils it will be observed that, on the average, slightly more than 50% of the added nitrogen plus that made available from the soil was recovered in the crop. This recovery figure agrees closely with the values commonly obtained in lysimeter experiments. The unrecovered nitrogen was either lost in the drainage water or as gas.

In the unlimed series the crop growth was less than in the presence of lime, and there was a somewhat greater release of nitrogen from the soil. Only about 29% of the available nitrogen was recovered in the crop. This value is even lower than that obtained in the Connecticut lysimeter experiments where much larger cuantities were added to a sandy soil cropped to tobacco. Again we assume, as Lipman and Blair (28) had earlier, that most of the unrecovered nitrogen escaped through leaching. Low crop yields, due to high acidity, would of course favor leaching. It is also well to bear in mind that nitrites are very unstable in acid media and at pH values below 5.0 nitrogen may escape readily as nitrio oxide. This may have happened to some extent in these New Jersey cylinders.

Other experiments might be mentioned, if time permitted, which, in general, seem to indicate that nitrogen recovery results, obtained in field experiments, are not greatly different from those reported from lysimeters. There is, however, one important difference between experimental data and practical field results that is sometimes overlooked. In most lysimeters, the water that falls on the soil stays there. There is no runoff. Likewise, experimental field plots are usually located on nearly level soil where the runoff is below average. Under practical field conditions, especially where the soil surface is rolling, it would be logical to expect less loss of nitrogen by leaching than the experiments discussed here would indicate. I decreased rate of removal would give the crop more time to assimilate it. On the other hand, it would allow more opportunity for gaseous losses to occur.

#### Greenhouse Experiments at Beltsville, Maryland

Is a supplement to the studies reported above, it is interesting to see what information greenhouse studies can contribute to the solution of the soil nitrogen balance enigms. The ideal experiment for this purpose is one where several applications of nitrogen were made to the same soil, several non-legume crops grown, and all crops and soils analyzed. Few greenhouse experiments, reported in the literature, meet these requirements. Only two, which were conducted by Pinck and coworkers (42, 43) at Beltsville, will be discussed here.

In one of these experiments (12), five successive green manure crops were grown on an Evesboro loamy sand soil to various stages of maturity, and then incorporated with the soil. If ter each green manure crop a crop of wheat, or Sudan grass, was grown and the tops harvested. Nitrogen in the form of urea was added at different rates, part to the green crop and part to the harvested crop.

When the nitrogen recovery data from all of the treatments are plotted against total nitrogen added, the results fall near a straight line. The slope of this line shows that for every unit of nitrogen added, the unaccounted-for nitrogen amounted to about 18%. The few small gains of nitrogen at the lower nitrogen levels may indicate nonsymbiotic fixation but more likely are merely within the normal experimental error.

In the second greenhouse experiment, reported by the same authors (13), the technique was similar, except that the green crops were grown in the field and added to the soil together with urea. A few pots received applications of urea, sodium nitrate, and cottonseed meal without additions of plant materials. The total number of treatments was 33, all in duplicate. Five successive additions were made and a crop of either wheat or Sudan grass was grown after each addition of green crop.

The straight-line graph of these data shows that for every unit of nitrogen added, regardless of its form, the unaccounted-for nitrogen amounted to about 1h%. A smaller loss in this experiment might be expected since a large percentage of the nitrogen was supplied as plant materials.

The average loss of 16% of the nitrogen in the two greenhouse experiments agrees surprisingly closely with the value of 20% for the cropped lysimeters. In the greenhouse studies there were, of course, no leachates to collect and analyze. Furthermore, soil sampling could be done much more accurately. On the other hand, there was a greater chance for denitrification in the greenhouse due to possible temporary waterlogging of the soils.

Losses of nitrogen by volatilization. -- Since volatilization is apparently important and not well understood, we shall consider this subject in some detail. Such losses may occur through at least five channels or mechanisms. These are:

- 1. Is ammonia.
- 2. As oxides of nitrogen.
- 3. As nitrogen gas by chemical reaction.
- 4. As nitrogen gas by bacterial denitrification.
- 5. As organic substances from plants.

Losses as ammonia. -- There is essentially universal agreement among investigators (24, 27, 33, 50, 51, 57) that under suitable conditions ammonia is rapidly lost from soil by volatilization. Such losses may amount to 10 to 25% or even more of the ammonia added or formed. The main established facts are:

- 1. Barely detectable losses may occur at pH 6 to 7 but they increase markedly at higher pH values.
- 2. Losses from wet soils are likely to be small but are very high if an alkaline soil, containing much a mmonia near the surface, is dried.

3. Losses increase with temperature.

4. Losses are greatest in soils of lowexchange capacity.

5. Icsses may be high where nitrogenous organic materials are allowed to decompose on or near the soil surface, even if the soil is acid. As the organic materials decompose, the ammonia formed raises the pH locally and permits volatilization. This partially explains the low recoveries in the crop of nitrogen added as manure, when it is spread on the soil surface.

Losses of oxides of nitrogen. -- Nitrogen may escape from soils as either nitric or nitrous oxides under certain limited conditions. Such losses may occur in considerable quantities from both acid and alkaline soils.

Nitric oxide, as is well known (3, 17, 18, 19, 46, 52), is formed rapidly from nitrous acid under acid conditions. Such decomposition of nitrites becomes appreciable at a pH of about 5.0, and the rate and extent of decomposition are greatly accelerated with increase in acidity. Most of the nitrio oxide formed is normally oxidized chemically to nitric acid or is absorbed by soil organic matter, but some of this gas escapes to the air. This lack of stability of nitrous acid is doubtless one of the main reasons for negative nitrogen balance sheets commonly obtained when working with acid soils. Microorganisms can contribute to this source of nitrogen loss through the formation of nitrites, but probably do not produce (56) nitric oxide directly.

Nitrous oxide is also commonly formed in soils, if nitrates are present and oxygen is very deficient. In well-aerated soils only traces, if any, of this gas are formed. These facts have been demonstrated just recently in three separate laboratories, namely, at Irizona, California, and Cambridge. Both Idel (1) and Arnold (6) consider that the soil is the probable source of the nitrous oxide found in the atmosphere. Wijler and Delwiche (56) found that under most soil conditions nitrous oxide was the major product of denitrification. It was, however, readily reduced to free nitrogen gas in soils of pH7 and above, but not under acid conditions.

Losses as nitrogen gas by chemical reaction. -- Many claims (5, 58) have been made that in both plant juices and soils nitrous acid reacts with reduced forms of nitrogen, such as mino acids and ammonia, to form nitrogen gas. This reaction proceeds rapidly and quantitatively in a Van Slyke apparatus in the presence of glacial acetic acid and in an atmosphere of nitric oxide. Recent work (3, 4, 56) has shown, however, that there is little likelihood that this reaction occurs to any appreciable extent under conditions commonly occurring in nature. At pH values where the reaction can occur at an appreciable rate, namely 5 or lower, conditions for nitrite formation by both oxidation and reduction are not favorable. Even if formed, the nitrites are much more likely to

decompose to form nitric oxide then they are to react with amines or ammonia to form nitrogen gas. We must, therefore, conclude that there is no conclusive evidence at present that nitrogen is lost in more than minor cuantities from either soils or plants by the Van Slyke reaction.

Losses as nitrogen gas by bacterial denitrification. -- It seems to be generally agreed among soil bacteriologists that most of the gaseous losses of nitrogen from soils, other than as ammonia, are brought about by denitrifying bacteria. These losses occur chiefly as free nitrogen gas and nitrous oxide. Under strictly anaerobic conditions nitrite and nitrate-nitrogen may be almost completely volatilized in a comparatively short time. The experiments reported recently by Jones (25), show this very strikingly. Where sodium nitrate was added to an air-dried soil, which was then brought up to optimum moisture and incubated anaerobically, about 80% of the nitrogen was volatilized in 3 days. Denitrification proceeded almost as fast where the sole source of energy was soil organic matter as where 0.5% sucrose was added. The rate of gas evolution would undoubtedly have been considerably more rapid if fresh soil had been used.

The rapidity with which denitrification occurs can be shown even more strikingly if pure cultures of denitrifying bacteria are used. Using the Warburg respiration technique, for example, quantitative conversion of nitrite nitrogen into gas may be observed during a period of 2 or 3 hours in the absence of oxygen. Where oxygen is present the rate of evolution of nitrogen gas is markedly retarded. For many years it was rather commonly believed that bacterial denitrification occurs only in soils that are completely anaerobic. Several recent papers (9, 11, 15, 34, 48, 56) have, however, generally agreed that although the process is markedly inhibited by oxygen it is not stopped completely. It is not, however, easy to demonstrate nitrogen evolution in soils that are kept well aerated. Neither is it easy to account for all of the nitrogen added even if tracer techniques are used (32, 56). This subject needs further investigation.

Losses as organic substance from plants. -- A few organic substances, such as methylamine, trimethylamine, hydrocyanic acid, and nicotine, are known to be exuded from plants and a portion of these compounds may be lost by volatilization. Nitrates, nitrites, and ammonia, also commonly occur (58) in plant exudates but most of this nitrogen returns to the soil. Data on the quantities of nitrogen lost to the air from plants are meagre but they are believed to be small.

When we consider the various channels through which nitrogen can be volatilized, it is not surprising that soil nitrogen balance sheet often fail to balance. One might almost be tempted to ask why the unaccounted for nitrogen figures are not higher than the 15% average value previously mentioned for lysimeters. Under

conditions where soils are likely to be less aerobic than they are in lysimeters, larger gaseous losses would certainly be expected. In the presence of nitrates this might occur:

1. In rice paddies,

2. In heavy soils that are poorly drained,

3. In normal soils during wet periods, or

4. In normal soils where fresh organic matter is abundant.

Large losses would also be expected as a result of the volatilization of ammonia from normal soils where the pH is 7 or above, and ammonia is added, or being formed at a rapid rate.

In this connection it is of interest to refer to the dry land soils of the United States where leaching rarely occurs. In such regions it has been shown repeatedly that many of these soils have lost far more nitrogen during the past 50 years than has been removed in the crops — usually 2 to 3 times as much. Presumably most of this loss has been through volatilization, but positive proof of this is lacking. Since most of these soils are basic, or only slightly acid, the chief loss may be as ammonia.

In general, this discussion has emphasized the ease with which nitrogen is lost from soils. Mineral nitrogen, whether added as fertilizer or formed from soil organic matter, will not long remain in the soil in this form. If it is not assimilated by higher plants it will usually be lost through leaching or by volatilization. Such losses can be minimized by providing sufficient carbon to combine with it to form soil organic matter. But even this fixing of the nitrogen by carbon is only temporary unless there is a permanent change in the agronomic system that will permit the establishment of a new equilibrium, and a higher organic matter level.

### Gains of Nitrogen from the Fir by Means other than Legumes

It would not be well to conclude this discussion of nitrogen balance sheets without at least a brief reference to some of the suigmas connected with soil gains in nitrogen. So far as the present discussion is concerned, we can omit nitrogen fixation by legumes, for their importance in maintaining and increasing soil nitrogen is well appreciated, even if the exact quantity of nitrogen fixed is seldom known.

The chief enigma centers around the question: How important is non-symbiotic nitrogen fixation in soils? From time to time claims have been made that under certain conditions, especially in warmer climates, fixation by free-living bacteria is adequate to meet most or all of the crop needs indefinitely. There are, however, few, if any, instances where adequate proof of such statements can be found. It the present time nearly all workers (23, 40), at least those outside of Russia (2), seem to consider that the quantity of nitrogen fixed annually in the average soil by free-living organisms is small. There are some

indications that grasslands may occasionally be an exception since several workers (20, 26, 30, 35, 45, 54, 55) have reported annual fixations of 20 to 40, and even more, pounds per acre. Such results are seldom convincing. When a large fixation is obtained it is likely to be emphasized, whereas a loss or small gain may scarcely be mentioned. Such negative results are not uncommon. Nitrogen increases in sod<sup>8</sup> that may seem real may be merely apparent because of a variety of reasons including:

1. Errors of soil sampling and analysis.

2. Inadequate allowance for additions of nitrogen in rainfall.

3. Failure to keep the grass free from all legumes.

4. Insufficient protection against the collection of extraneous material, especially due to blowing.

5. Lack of certainty that nitrogen is not obtained from the subsoil or ground waters.

It is also possible that some ammonia and oxides of nitrogen may be absorbed from the air as suggested by Ingham (21), and others. Furthermore, when a grass plot is located along side of a cultivated plot the marked difference in nitrogen content of the soils after several years may indicate a fixation that did not occur.

On the basis of present information we may conclude that, while there is a possibility that nitrogen fixation in grass sods may be important, we are not justified in accepting this idea until we have much more reliable data than are available at present.

Since accurate data on nonsymbiotic nitrogen fixation under field conditions are not available, an evaluation of the process must be based chiefly on laboratory data, and on our general knowledge of the metabolism and growth requirements of the organisms involved. Such information would certainly indicate that Azotobacter fixes little nitrogen under field conditions. This conclusion is based chiefly on the following facts:

- Azotobacter seldom occur in large numbers in soils, and are usually completely absent from soils that are appreciably acid.
- 2. They have high energy requirements and the energy sources must be simple. Crop residues become available only as a result of attack by other organisms that use most of the energy themselves. Even if sugar is supplied under pure culture conditions, Azotobacter seldom fixes more than a pound of nitrogen per 100 pounds of carbohydrate.

3. Azotobacter do not thrive in the rhizosphere (12), and even if they did, the available energy supply for root secretions is probably not large.

4. Nitrogen fixation is inhibited by soluble forms of

nitrogen in the soil.

The growth requirements of the anaerobes would indicate even less fixation in normal soils than is brought about by Azotobacter.

Nitrogen fixing blue-green algae may be of far greater importance then / zotobacter under some special conditions. In an environment such as a rice field, for example, several recent studies (10, 41, 49, 53) show that these organisms are commonly abundant and active in fixation. They are not, of course, limited by lack of energy supply, as are the bacteria. They do, however, require much moisture, a neutral soil, and a fairly warm climate. These growth requirements would indicate that they are not of great importance in normal soils, but quantitative data in support of this viewpoint are entirely lacking.

#### Concluding Statement

From the facts presented it is obvious that regardless of years of research, we can seldom draw up a soil nitrogen balance sheet for a field soil that is accurate. This is, of course, because we usually lack cuantitative data for some of the major items that we know are involved in the calculations. We lack the data because of the experimental difficulties encountered in obtaining them. It is impossible, or at least impractical, to account for all soil gains and losses in a single experiment conducted under reasonably normal growth conditions. In order to obtain accurate values for some sources of gains and losses it is necessary to make the experimental conditions more and more artificial. We then wonder how closely the data obtained apply under field conditions.

It would seem, however, that the enigma of soil nitrogen balance sheets is much less of an enigma now than it was a few years ago. If the balance sheet doesn't balance it is usually because the nitrogen values for either leaching or volatilization, or both, are too low. There is need for more and better experimental data on both sources of loss. The leaching and erosion losses should be determined for undisturbed soils under various conditions with respect to soil, crop, climate, and topography. On the other side of the balance sheet, we shall also hope for convincing experimental support for the claims for large fixations of nitrogen in tropical soils and grasslands through channels other than legumes.

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